

BEAMLINE

X18B

PUBLICATION

R.V. Hull, L. Li, Y. Xing, and C.C. Chusuei, "Pt Nanoparticle Binding on Multiwalled Carbon Nanotubes", *Chem. Mater.*, **18**, 1780–1788 (2006).

FUNDING

American Chemical Society Petroleum Research Fund; Foundation for Chemical Research, Inc.; Missouri Research Board; UMR Intelligent Systems Center

FOR MORE INFORMATION

Charles C. Chusuei, Chemistry Department, University of Missouri-Rolla
chusuei@umr.edu

Characterizing the Surfaces of Carbon Nanotube Fuel Cell Catalysts

R.V. Hull¹, L. Li², Y. Xing², and C.C. Chusuei¹

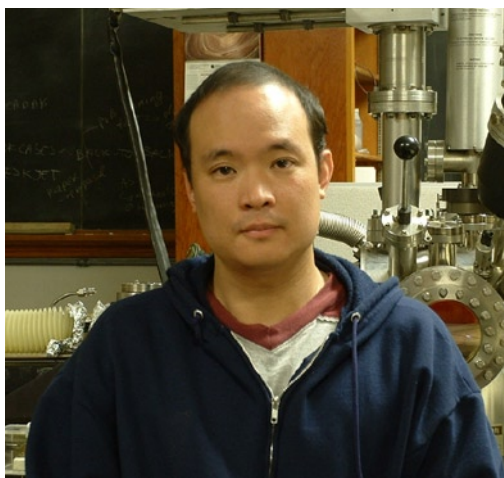
¹Department of Chemistry and ²Department of Chemical and Biological Engineering, University of Missouri-Rolla

Characterizing the surface structure of catalyst materials is important for the improvement of current fuel cell technology, which promises to deliver an environmentally benign means of energy production. Using x-rays produced at the National Synchrotron Light Source (NSLS), researchers at the University of Missouri-Rolla (UMR) were able to detect the presence of PtO_x at the outer-most perimeters of a potential catalyst: platinum nanoparticles tethered to carbon nanotubes. At the same time, they determined that its bulk composition was predominantly metallic.

Fuel cells are devices capable of generating electrical energy directly without involving a thermal cycle that typically release greenhouse gases, such as CO and NO_x, into the atmosphere. Today, burning coal is still the primary and most efficient (with regard to power density) means of electrical energy production in the United States. New information obtained from a study performed at the NSLS may help catalyst researchers design improved fuel cell devices that can compete with current fossil fuel technology.

The active material on the carbon-nanotube supports consists of tiny platinum particles on the order of a few nanometers in diameter, which are deposited on the carbon surface. The deposition of these particles on the nanotubes has been found to enhance the electrocatalytic activity for direct methanol fuel cells (DMFCs) by as much as 48% relative to carbon black, but the underlying reasons for this observation have yet to be fully described. The exact relationship between the interfacial structure of these carbon-supported metal nanoparticles and their subsequent chemical activity has long mystified catalyst scientists.

Researchers from the University of Missouri-Rolla (UMR) used x-rays at NSLS beamline X18B to characterize the interfacial structure of platinum particles tethered to carbon-nanotube (CNT) catalyst surfaces. Graduate students Robert V. Hull and Liang Li and professors



Charles Chusuei

Charles C. Chusuei and Yangchuan Xing in the departments of Chemistry and Chemical and Biological Engineering at UMR collaborated on the study. The results of the work appear in the April 4th, 2006 issue of *Chemistry of Materials*. The paper describes how the researchers used the extended x-ray

absorption fine structure (EXAFS) technique in conjunction with x-ray photoelectron spectroscopy (XPS) (performed at UMR) to probe the surface and subsurface structures of the nanoparticles. They aimed to show evidence for the coordination of the platinum to oxygen atoms attached to the surface of the nanotubes (Pt-CNTs), which were functionalized with ketone, ester, and hydroxyl groups.

XPS is sensitive to probing approximately 50–100 Å deep while EXAFS is sensitive only to the first few atomic layers of the metal particles being probed. Comparisons of the two sets of spectra show that both metallic and oxidized platinum were present. It was discovered that the outer-most structure of the particles consisted of an oxide, PtO_x, while the bulk of the nanoparticles was fully metallic. The XPS of the Pt 4f orbital showed a binding energy of 71.4 eV, indicative of the bulk metallic structure of the platinum nanoparticles (**Figure 1**). The nearest-neighbor distances for the metal nanoparticle tethered to the nanotubes were observed at distances of ~1.78 Å — much too short for the expected ~2.77 Å

distance between metallic platinum atoms (**Figure 2**), which signified Pt–O at the outermost perimeter of the clusters. This structure accompanied the increased DMFC ac-

tivity observed. In addition to the dried powder catalyst materials, experiments were performed on the Pt-CNTs under aqueous solution environments to simulate the

working conditions of the fuel cell, which exhibited the same surface structure as the dry powdered form.

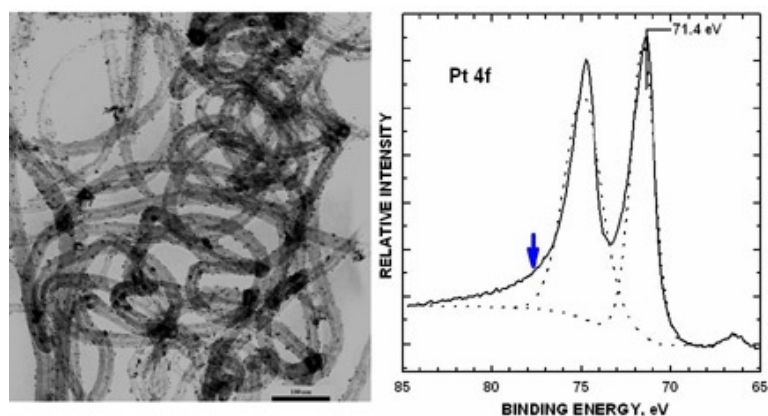


Figure 1. Pt 4f core level XPS spectrum (right panel) of nanoparticles tethered onto multiwalled carbon nanotubes; arrow denotes evidence for Pt(II/IV) oxidation state albeit small in amount. Left panel shows a transmission electron micrograph of Pt nanoparticles ~ 3.5 nm in diameter; the scale bar shown corresponds to 100 nm.

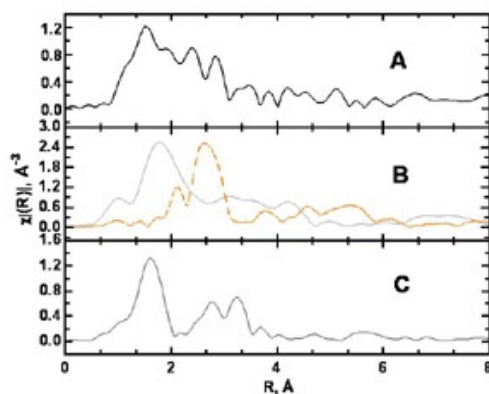


Figure 2. Pt L_3 edge EXAFS Fourier Transformations of (A) Pt-CNTs in an aqueous colloidal suspension; (B) Pt-CNTs in dry powder-like form (solid gray line; Pt foil scan shown as a dotted, orange spectral line); and (C) a PtO_2 standard.